United States Environmental Protection Agency Air and Energy Engineering Research Laboratory Research Triangle Park NC 27711

Research and Development

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Project Summary

Prevention Reference Manual: Chemical Specific, Volume 3: Control of Accidental Releases of Hydrogen Cyanide (SCAQMD)

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The South Coast Air Quality Management District (SCAQMD) of Southern California has been considering a strategy for reducing the risk of a major accidental air release of toxic chemicals. This strategy, intended to guide both industry and communities, consists of monitoring activities associated with the storage, handling, and use of certain chemicals. The hydrogen cyanide (HCN) manual summarizes technical information that will aid in identifying and controlling release hazards (specific to the SCAQMD) associated with HCN.

Because HCN has an IDLH (immediately dangerous to life and health) concentration of 50 ppm, it is an acute toxic hazard. The manual identifies the potential causes of accidental releases that apply to processes using cyanides in the SCAQMD and also describes measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices; prevention, protection, and mitigation technologies; and operation and maintenance practices. Conceptual cost estimates of examples of these measures are provided.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In 1985, the South Coast Air Quality Management District (SCAQMD) conducted a study to determine the presence, quantities, and uses of hazardous chemicals in the SCAQMD, which consists of Los Angeles, Orange, San Bernardino, and Riverside Counties. The resulting report, "South Coast Air Basin Accidental Toxic Air Emissions Study," outlined an overall strategy for decreasing the potential for a major toxic chemical release.

The hydrogen cyanide (HCN) manual, which contains technical information on the prevention of accidental releases of HCN, discusses storage and handling practices and process operations involving cyanides as they are used in the SCAQMD that could result in an accidental release. Although HCN itself is not used in the SCAQMD, its salts are used in electroplating operations. In the electroplating industry cyanides are used in plating solutions for certain metals and in cleaning solutions used to prepare metal surfaces for plating. Here the cyanide is present only in the salt form, most commonly as sodium cyanide. HCN is not directly used in the SCAQMD in the plating industry.

Potential Causes of Releases

Cyanide solutions can be used safely in the plating industry, though the industry has been moving away from their use since substitutes are available for many metals in certain applications. Though cyanide salts are toxic, since they have very low vapor pressures in solution or in the solid form, they are not as hazardous as HCN. However, small amounts of HCN will be present whenever a cyanide salt or salt solution is used. Large amounts of HCN could be generated if acid were added to a cyanide salt solution, but an accidental release of HCN from a cyanide-based plating bath appears to require adding a large amount of acid.

Failures in or problems with a chemical process, equipment, or operating and maintenance procedures can cause accidental releases. Since very little automatic process control is used in typical plating operations and since the solution compositions within a process are typically monitored and adjusted manually, any error in adjustment leading to an HCN release would most likely be caused by operator error.

An accidental release related to equipment failure might occur if a spilled cyanide solution came in contact with a strong acid. Examples of equipment failure that could cause spills are:

- Failure of a bath resulting in a spill of cyanide-containing solution. The failure could be caused by excessive stress, external loadings, or corrosion.
- A spill of cyanide-containing solution from a bath caused by a pump or pipe failure.
- A fire, resulting in an accidental release of cyanide. Destruction of cyanide salt containers by fire, combined with water from a sprinkler system, could result in a sodium cyanide runoff. Sprinkler water could also cause a tank overflow and mixing of acid and cyanide baths.

Human error could lead to an accidental release; e.g.:

- Overfilling of baths resulting in an improper mixture of acidic and cyanide solutions.
- Incorrect addition of acidic raw materials to a cyanide bath.
- Incorrect transfer of liquid from an acid bath to a cyanide bath or vice versa.
- Use of a carbon dioxide (CO₂) fire extinguisher on a fire where cyanide salt or solution is present, resulting in an accidental release of HCN. CO₂ is a weak acid, however, and large quantities would be necessary to create an accidental release of HCN.

Hazard Prevention and Control

Prevention of accidental releases requires careful consideration of the design,

construction, operation, and protective systems of facilities where HCN is stored and used.

Few options appear to exist in process design for reducing the potential of an accidental release from plating processes. One method would be to switch to a noncyanide-based process if economics allow it and if the non-cyanide process is adequate for the intended application. The only control system in a plating operation is likely to be temperature control on some of the baths. Transfers, monitoring, and composition adjustment are typically done manually.

From the perspective of accidental release prevention, pH control of cyanide-based plating solutions is very important, and also typically accomplished manually. Since plating solutions are highly buffered, they are resistant to pH change. It might be difficult to automate pH control, but if such controls were incorporated into the plating process, a backup system should be used to protect the process from control system failures that result in low pH.

Physical plant design considerations include equipment such as vessels, pipes, valves, instrumentation, siting and layout, and transfer/transport facilities. Foundations, dikes, walls, flooring, and other supports should be constructed from materials resistant to attack by the chemicals used in the plating process. For example, "acid brick" combined with chemically resistant mortar is a reliable material to use for corrosion protection. Tanks must be constructed of or lined with a material resistant to chemical attack such as plastic, stainless steel, lined carbon steel, or lined precast or pouredin-place concrete.

Facilities and equipment should be located so as to reduce plant and public personnel exposure in the event of a release. Inventories of solid cyanide salts should be separated from inventories of acid. Cyanide salts should be protected from contact with moisture, and adequate drainage or diking should be available to prevent runoff or spills from leaving the building. Overflows or leaks from one bath should not be able to contaminate another bath.

The two types of protection technologies for cyanide-based plating facilities are enclosures and scrubbers. Ventilation systems and individual hoods, or a combination of these, are used to capture vapors from areas where HCN might be generated. For most cyanide plating operations, scrubber systems may be a level of protection out of proportion to the hazard, but they could be used when extreme precautions are needed. Incineration or flaring may also be applicable to control HCN vapors.

Mitigation techniques, to reduce the consequences if a release of HCN occurs, include physical barriers, water sprays and fogs, and foams. Secondary containment systems such as diking are used to contain accidental liquid spills and reduce the rate of evaporation by decreasing the surface area of the spilled liquid. For plating facilities, diking could be effective around acid storage tanks to isolate spills from dry cyanide storage areas.

Employees of plating facilities should be trained in important aspects of handling cyanide salts and solutions, especially the dangers of excess acidification of these solutions, and should thoroughly understand maintenance and emergency procedures.

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The complete report, entitled "Prevention Reference Manual: Chemical Specific—Volume 3: Control of Accidental Releases of Hydrogen Cyanide (SCAQMD)," (Order No. PB 87-227 062/AS; Cost: \$13.95, subject to change) will be available only from:

National Technical Information Service 5285 Port Royal Road Springfield, VA 22161

Telephone: 703-487-4650 The EPA Officer can be contacted at:

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